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Site Occupancy/Valence Measurements Using Channelling and Related Effects in Microanalysis

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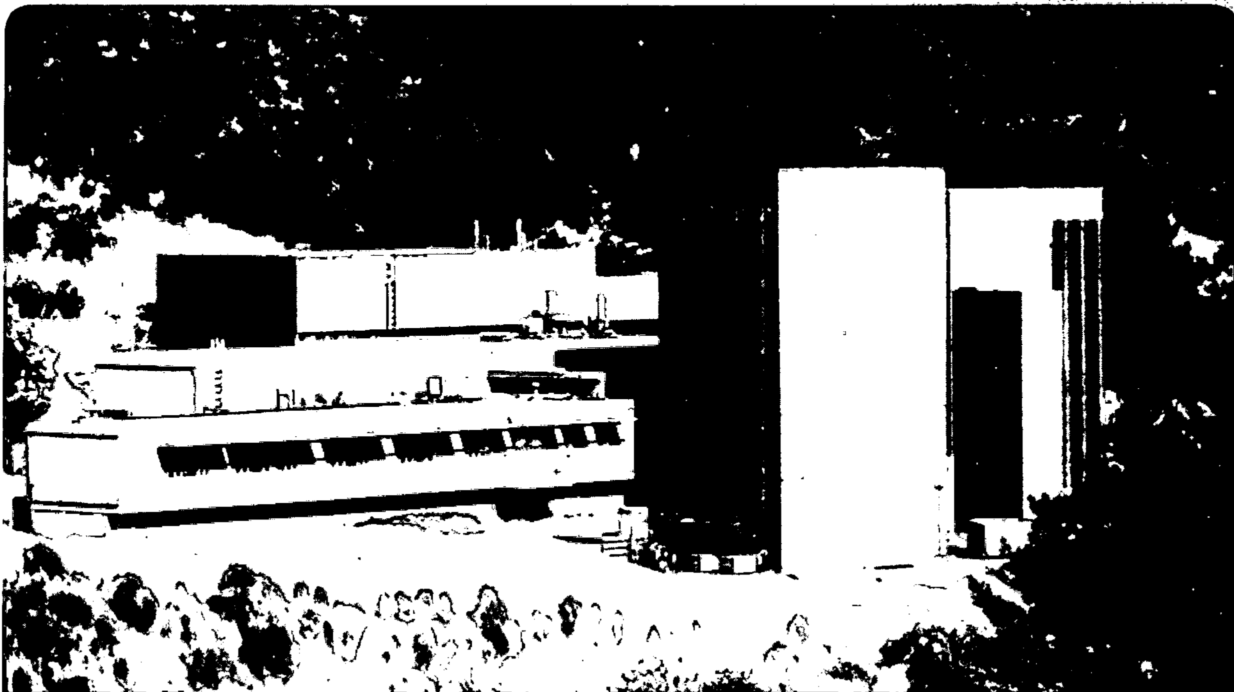

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SITE OCCUPANCY/VALENCE MEASUREMENTS USING CHANNELLING AND RELATED EFFECTS IN MICROANALYSIS

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ABSTRACT

The current status of a novel crystallographic technique to determine specific-site occupations of elemental additions in crystalline materials, using the channelling or Borrman effect in electron diffraction is discussed. This technique is based on the effect of incident beam orientations on the intensities of either the characteristic x-ray emissions or the characteristic electron energy-loss edges. In general, this technique is in good agreement with other well established methods such as x-ray and neutron diffraction but has superior spatial resolution (~10-40nm). It involves no adjustable parameters, external standards or special specimen preparations; can distinguish neighbours in the periodic table; is very accurate and is applicable to trace elemental concentrations (0.2-0.3 wt % or 10^{25} atoms/m^3). In the EELS formulation the technique can also provide specific site valence information. Finally, its applicability to the study of site occupancies in magnetic materials (spinels, $Sm_2(Co,TM)_{17}$ alloys, $(Y,RE)_3Fe_5O_{12}$ epitaxial films, etc.) has been well demonstrated.

1. INTRODUCTION

The synthesis of magnetic materials to achieve better performance always involves a careful characterization of the microstructure and an understanding of its implications on the properties as well as the mechanisms influencing them. Electron microscopy has played an important role in this endeavour as the interaction of a fast electron accelerated through kilovolt potentials in a TEM with a thin foil specimen produces a variety of signals that can be measured with appropriate detectors to provide a wealth of information about the material [1,2]. In particular, by monitoring the inelastically scattered primary electron distribution either as a function of energy or momentum (electron energy-loss spectroscopy), one can obtain information related to the chemistry, bonding and electronic structure of the sample [3]. Alternatively, the de-excitation or secondary processes such as characteristic x-ray emissions, monitored by either solid state detectors or detecting crystals, find wide application in microanalytical characterization. A principal application of both these spectroscopies in the TEM/STEM environment

has been largely in the area of chemical microanalysis where the characteristic x-ray peak or electron energy-loss edge intensities are interpreted in terms of the composition of the sample.

However, for crystalline or polycrystalline materials, both the characteristic energy-loss edge and the x-ray peak intensities show a strong dependence on the orientation of the primary beam. In general, an incident plane-wave of electrons under conditions of strong dynamical scattering sets up a standing wave within the crystal. For certain incident beam orientations, the standing wave modulation across the unit cell is such that its maximum coincides with a particular crystallographic site containing a specific atomic species and producing an enhancement of the corresponding edge/peak intensities. This orientation dependence of the emission product (EDXS) as well as the energy-loss electrons in transmission (EELS), has been developed into a powerful crystallographic technique for specific site occupancy/valence determinations called ALCHEMI or atom location by channelling-enhanced microanalysis (see[4], for a recent review). In the case of EELS, the experimental arrangements are more flexible, as both the incident and collection directions are selected independently, and the channeling and blocking effects are incorporated in the analysis [5]. In general, the method pre-supposes strong localization of the scattering event and has been widely used both for the measurements of site occupancies [6-8] and small atomic displacements from the perfect lattice site in imperfectly ordered alloys [9]. Needless to say, site occupancies/valences play an important role in determining the properties of magnetic materials. In particular, for materials synthesized either by liquid phase epitaxial or sintering processes, it is essential to achieve a suitable microstructure with the correct oxygen content and distribution of cations with appropriate valences.

2. PHYSICAL DESCRIPTION OF THE TECHNIQUE

A typical experimental arrangement for the characteristic x-ray emission case, in the planar channelling geometry, is shown in Figure 1a. The characteristic x-ray signal is measured as a function of incident beam orientation by a fixed detector whose position with respect to the sample is defined by the take-off angle, ψ. The projected crystal structure with the standing-wave pattern of the primary beam, set up as a result of the strong dynamical scattering, is shown in Figure 1b. For a systematic or planar channelling condition, the wavefield of the incident electron in the crystal is two-dimensional (i.e. constant in a direction normal to the page). The modulation of the standing wave on specific crystallographic planes is then a function of the incident-beam orientation. Highly localized secondary phenomena such as characteristic x-ray emissions are also a function of these modulations of the primary beam (Figure 1c). For a particular favourable orientation (θ_1), the Bloch waves are maximized on the A planes with a concomitant increase for the elements occupying the sites Δ. For the other favourable orientation (θ_2), the maximization is on the B planes with a corresponding increase for the elements occupying the sites 0.

The development of a meaningful technique of quantitative site occupancy determinations, utilizing the above variations of the x-ray intensities with orientation, is then largely dependent on both the ability to determine these favourable orientations and to obtain an independent measure of the electron intensity modulations over the unit cell. For electrons accelerated through kilovolt potentials, the latter can be calculated using a dynamical many-beam theory [10]. However, the need for a theoretical prediction of the electron wave field in the crystal can be avoided by using the x-ray emission from a reference atom whose distribution in the host crystal lattice is known [6]. Further, as secondary emission processes are highly localized, these intensities are then proportional to the thickness-averaged electron intensity on specific atomic columns.

For a planar channelling or systematic orientation (a single row of spots are seen in the diffraction pattern) the crystal potential is averaged in two orthogonal directions normal to the excited systematic row. For the simplest case, a crystal with a layered structure, the appropriate systematic orientations can be determined by mere inspection [4]. For example, the spinel structure compounds (Figure 2) can be resolved in the [001] projection into alternating (400) planes of tetrahedral (Mg) and octahedral (Al) sites and hence a g = 400 systematic row at the second order Bragg diffraction condition can be easily seen to be appropriate for this kind of experiment. Now, if an *a priori* knowledge of the distribution of some reference elements in the host lattice is available, their characteristic x-ray intensities could be used to obtain a measurement of the thickness-averaged electron wavefield intensity on specific atomic planes. In the simplest case [6], the distribution of impurity or alloying additions is determined by an elegant method of ratios of their characteristic x-ray intensities with respect to those of the reference elements at two different orientations; i.e. at a channelling orientation and at a random non-channelling orientation defined such that no lower order diffraction vectors are excited. For a crystal such as the spinel, $MgAl_2O_4$ (Figure 2) consisting of two reference elements (Mg [a] on tetrahedral sites and Al [b] on octahedral sites), elements a,b lying exclusively on planes A, B respectively, the fraction of the unknown dopant (Fe, say) lying substitutionally on plane B, C_x is given by [6]

$$C_x = \frac{\dfrac{N_x^1}{N_x} - \dfrac{N_a^1}{N_a}}{\dfrac{N_b^1}{N_b} - \dfrac{N_a^1}{N_a}}$$

where the Ns are observed x-ray intensities for the elements a, b, x at the random orientations and the N^1s are the intensities for the same elements at the channelling condition.

If the structure is layered, but the requirement of the existence of at least one species that lies exclusively on one of the alternating planes is violated, more than one orientation along the same systematic row will be necessary to perform the analysis. The precise number of orientations required

will then be determined by the stoichiometry of the original compound and the actual distribution of the reference elements before alloying. An application of this approach to determine the site occupancies of transition metal additions in Sm_2Co_{17} alloys is reported in the literature. [8].

In the general case, where a projection of the crystal structure that separates the candidate sites into two planes each with a specific internal reference element cannot be found (for example the garnet structure, $I4_1/a32/d$), the appropriate planar-channelling conditions cannot be determined by inspection nor can the characteristic x-ray intensities be used as a measure of the thickness averaged electron intensity for any specific site. Then the characteristic x-ray emissions have to be calculated and the experimental intensities refined using a constrained least-squares method to determine the occupancies [7].

In conclusion, each problem of site occupancy to be solved in the planar channelling orientation has to be tackled separately, beginning by classifying the crystal structure into one of the three categories described above, and then proceeding with the appropriate formulation [4].

Electron channelling in the axial geometry represents an useful alternative to the experimental arrangement discussed thus far [11]. An electron beam incident close to the zone axis excites several low-index Bragg diffraction vectors, thus setting up several simultaneous standing waves [12]. For exact zone-axis orientations, this results in the electron beam being effectively channelled into columns with the current being maximized on atomic strings and with an accompanied increase in the characteristic x-ray emissions. Further, the channelling effects are considerably enhanced in the axial case [11,13]. This geometry is particularly suited for studying the degree of substitution of small quantities of dopants in a monatomic crystal. Details of the analysis, which are essentially the same as that for the planar channelling are given elsewhere [14].

In terms of practical applications, the axial geometry gives a stronger effect but in general it is difficult to find axial orientations which separate nonequivalent sites of the unit cell into distinct columns each containing a specific reference atom. On the other hand, finding planar orientations which separate candidate sites onto separate planes with specific reference elements is relatively straightforward for most crystal structures. Further, the planar method has demonstrated wide applicability in a variety of applications ranging from impurity site occupancy determinations in complex sublattices to specific site valence studies using EELS [4].

Characteristic x-ray emissions and the corresponding energy-loss edges should, in principle, show identical variation with the incident beam orientation. However, within the single scattering regime, applying the principle of reciprocity, it can be shown that the intensity in EELS for different site occupations can be effectively squared by choosing the position of the detection aperture and placing it at an appropriate part of the diffraction pattern to be energy analyzed [15].

3. DISCUSSION

3.1. Experimental Considerations. These site-occupancy measurements can be routinely carried out on most commercial electron microscopes equipped with either an energy dispersive x-ray detector or an electron energy-loss spectrometer. The methods are, of course, subject to all the limitations of the two individual spectroscopic methods. Moreover, no special specimen preparation methods are required. However, since all intensities are thickness-averaged, the distribution of impurities in the crystal should be uniform with depth. Any bending or thickness changes under the probe are unimportant as both the impurity as well as the reference elements are affected the same way by any local change in orientation.

3.2. Localization Effects. A basic assumption in performing these channelling experiments is that the inner-shell excitations concerned are highly localized at the atomic centers [6,7]. This localization is a function of the amplitude of thermal motion as well as the impact parameters <b>, defined as the expectation value of the distance at which a fast electron can transfer a specified quantity of energy to the core-electron. It had been estimated that for characteristic x-ray emissions of energy greater than 1keV, thermal vibrations provide the predominant influence on localization at room temperature [16]. However, recent calculations on localizations [17] based on a fully dynamical 49--beam (e,2e) model for ionization, for the <111> zone-axis orientation in GaAs, indicate that differences do occur for characteristic x-ray emissions in the 1-10keV range. Similar localization effects have been observed for Cr-Kα (5.4keV) in garnets [13] and for Sb/As in Si [11], both in the axial geometry. However, it is expected that the delocalization problem is more pronounced in the axial compared to the planar channelling case. This is because when many reflections are excited, contributions from Fourier components with large g vectors tend to delocalize the wavefield of the fast electron. In most cases, experimental correction factors (c-factor) for localization can be determined with relative ease. These c-factors are the ratios of the channelling effect for the higher energy Kα to the lower energy Lα lines [14].

Performing these channelling experiments at low temperatures has some significant advantages [18]--the scattering potential is less attenuated in higher order g-vectors leading to a greater variation in the electron beam intensities on the different sites. In addition, the amplitude of thermal vibration is considerably reduced. The latter is material dependent and no improvement is expected if the mean free path for phonon excitation becomes appreciably larger than the specimen thickness. For energy-loss experiments, it can be shown by a simple application of the uncertainty principle that the distance a fast electron can pass from the atom and still ionize it is inversely proportional to the momentum transfer associated with the inelastic scattering event. Simple calculations show [19], that by analyzing electrons scattered over large angles (i.e. large momentum exchange), the sensitivity can be greatly increased even down to 500eV losses as the corresponding inelastic scattering event would be more localized!

3.3. Spatial Resolution. The ability to use convergent probes and yet observe these channelling effects (within the constraints discussed above) makes it possible to routinely achieve a spatial resolution of 10-40nm. However, the spatial resolution is also determined by the statistics of the EDX detection process.

It is estimated that reasonable results can be obtained using a 20nm probe for a 10^{25} atoms/m^3 distribution of impurities. In order that the dynamical wavefunction be well sampled in depth the following simple criterion has to be satisfied [6]

$$\xi_g \, n \, A \geq 1$$

where ξ_g is the dynamical extinction distance for the reflection g, n is the uniformly distributed concentration and A is the projected area of the electron probe. Finally, the use of a higher brightness source, such as a field emission gun would, in principle, considerably improve the lateral spatial resolution of these techniques.

4. APPLICATIONS OF CHANNELLING ENHANCED MICROANALYSIS.

The techniques of channelling enhanced microanalysis or ALCHEMI, are not only well established but have found wide application in microstructural characterization. These applications can be broadly summarized as follows:

4.1. Specific site occupancy determinations. Indeed this is the most widespread application of this technique. Following a careful inspection of the crystal structure, with particular attention to the distribution of the candidate sites in the unit cells, the choice of the experimental arrangement (axial or planar channelling) can be made. For specific site occupancy studies, it is generally simpler to monitor the characteristic x-ray emissions, provided the localization corrections are incorporated if and when they are required. With this approach, impurity site occupancies for almost any crystal structure can be routinely determined.

Site occupancies determined by ALCHEMI have been compared with both x-ray and neutron diffraction with excellent results [20]. These channelling techniques are capable of resolving adjacent elements in the periodic table and site occupancies of trace element compositions can be resolved. The errors in these determinations can be in the range of 3-10% depending on which formulation is used. As described earlier, this high resolution technique requires no adjustable parameters unlike EXAFS/EXELFS and high resolution electron microscopy. A general discussion of the experimental impediments to ALCHEMI and sugggestions to overcome them are given elsewhere [4].

4.2. Specific Site Valence Studies. Because of the superior energy resolution for EELS (1-2eV using conventional LaB_6 filaments) when compared with EDXS (~ 150eV for 5.9 kV x-rays) it is possible to detect changes in oxidation states by the small chemical shifts observed in the EELS core edge features. For example a 2eV chemical shift is observed between Fe^{2+} and Fe^{3+} states. Combining this chemical shift with the selective enhancement of the different candidate sites, by the appropriate choice of incident beam orientation, it has been shown [21] that Fe^{3+} ions occupy octahedral sites while Fe^{2+} ions occupy tetrahedral sites in a naturally occurring chromite spinel (Figure 3).

4.3 Atomic Displacement Measurements. Alternatively, this method has also been used for the detection and measurement of static atomic displacements from the perfect crystal lattice site. Calculations taking into acccount the delocalization of the scattering event and the thermal vibration of the atom predict that displacements smaller than 0.01nm should be detected. Moreover, this resolution has been experimentally confirmed on studies of thin $In_{0.53}Ga_{0.47}AS$ epitaxial layers [9].

4.4 Other Related Studies. There are a variety of other manifestations of localized x-ray emissions with potential application in crystallography that need further investigation. For noncentrosymmetric crystals a pronounced intensity difference is observed along a polar direction for the g and -g reflections. This has been directly employed to determine the polarity of the crystal and to obtain structure factor phase information [22,23]. Further by exciting reflections inclined with respect to the specimen surface, a short wavelength modulation is set up in the depth of the film. It has been suggested [17] that such modulations should be able to resolve the species constituting the uppermost layer of the film.

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FIGURE CAPTIONS:

1. Physical principles of channelling enhanced microanalysis for specific site occupancy/valence measurements.

2. The spinel structure in the [001] orientation. In this projection the crystal structure is layered and can be resolved into (400) planes containing alternatively the tetrahedral and octahedral sites.

3. EEL spectra from a chromite spinel measured at two different channelling conditions (top). Selective enhancement of the octahedral site (a) and the tetrahedral site (b) can be observed. Details of the Fe $L_{3,2}$ edge for the same two orientations (bottom). The 2eV chemical shift makes it possible to confirm that the Fe^{3+} ions predominantly occupy the octahedral sites.

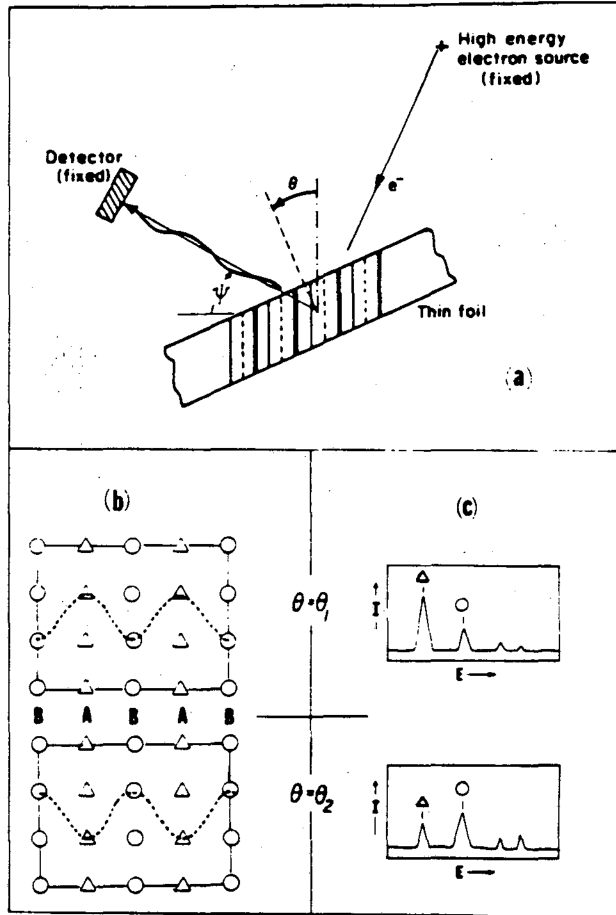

Figure 1

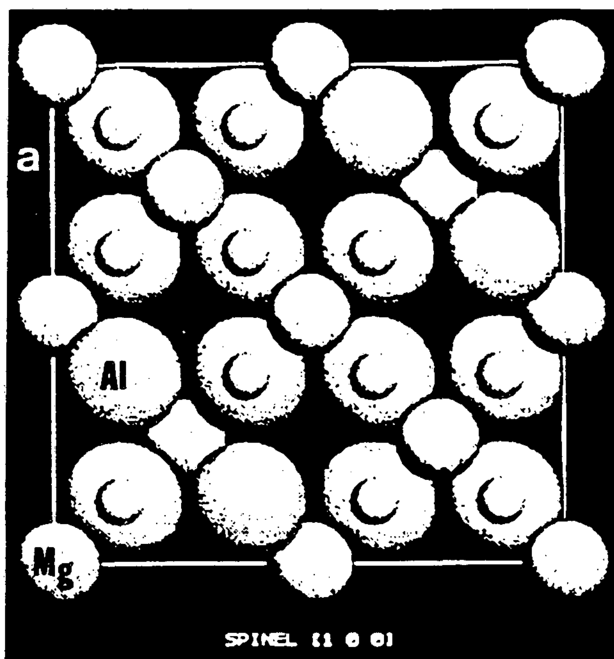

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Figure 2

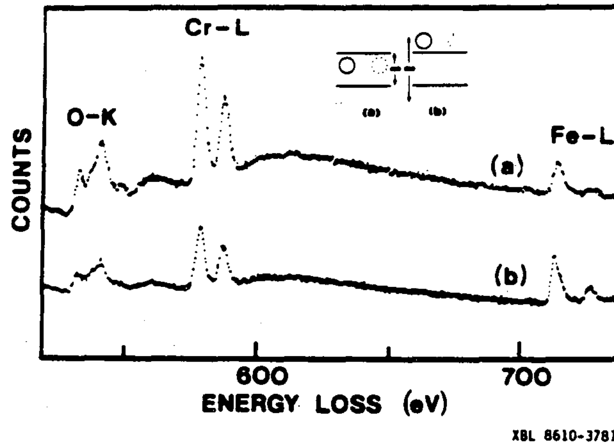

Figure 3a

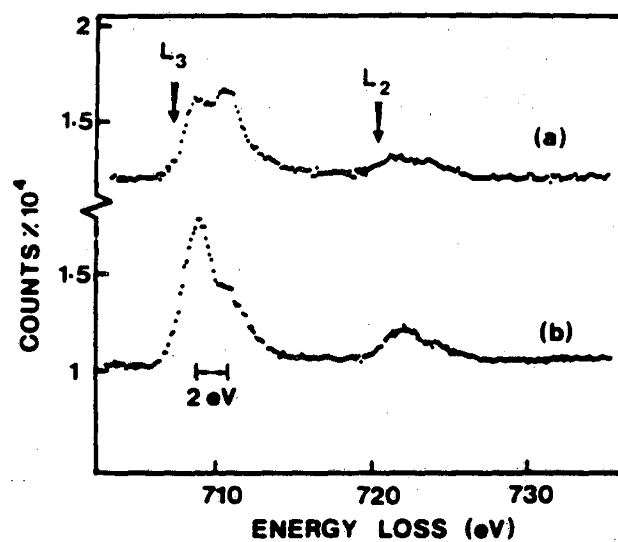

Figure 3b

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